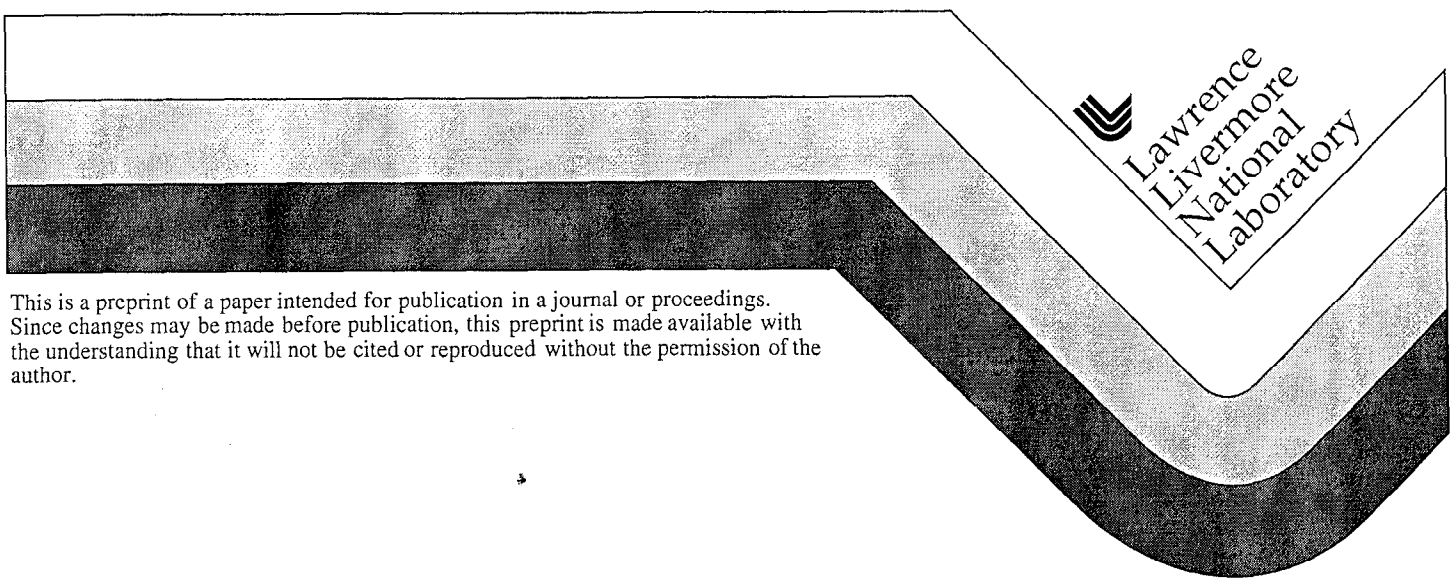
UCRL-JC-133762
PREPRINT

Non-Destructive Analysis of Organic Hydrogen Getter

David M. Chambers
James D. LeMay
Heather A. King

This paper was prepared for submittal to the
22nd Aging, Compatibility and Stockpile Stewardship Conference
Oak Ridge, TN
April 27-30, 1999

March 26, 1999



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Non-Destructive Analysis of Organic Hydrogen Getter

David M. Chambers and James D. LeMay
Lawrence Livermore National Laboratory

Heather A. King
Allied Signal FM&T

Abstract

We have developed both static and dynamic sampling approaches to monitor percent saturation and deuteration of 1,4-bis(phenylethynyl)benzene (DEB). To develop this method, it was necessary to separate and identify all partially saturated cis and trans isomers and developed algorithms to determine percent deuteration from the isotope distribution. The advantage of this approach is that the sample remains hermetically sealed in a protective headspace vial and is not destroyed.

Background

At this time, the weapons program needs an improved analytical method to characterize organic hydrogen getters. Although different aspects of getter material analysis have been addressed, none of these methods provides sufficient specificity, selectivity, and sensitivity needed for a complete characterization. Ideally, a method should: (1) distinguish the organic getter from its complex matrix; (2) discriminate hydrogen versus deuterium saturation; (3) resolve cis and trans isomers; (4) be quantifiable; (5) maintain sample integrity before and during analysis; (6) minimize sample work-up; and (7) be fully automated. The organic getters are fairly robust and exhibit considerably different melting points between the unsaturated and saturated forms. These characteristics are important because they permit the use of relatively high-temperature-extraction and -separation procedures that may be used to isolate targets from each other and any matrix. For example, one of the new organic hydrogen getters, 1,4-bis(phenylethynyl)benzene (DEB), has a melting point of 179°C, whereas its saturated form has an 87°C melting point.

New Sample Introduction Approach

Although it is impractical to assume that one analytical method can satisfy all these criteria, we believe that coupling several on-line techniques might bring us very near this goal. In addition, a number of sample collection and introduction techniques have been introduced as enhancements to the current state of the art. One sampling approach that has benefited from recent developments is equilibrium headspace analysis. For such analysis a material is placed in an inert, airtight environment and heated to outgas target compounds. The advantage of this approach is that it requires no sample preparation, can preserve the material in a non-reactive environment, and minimizes contamination. There are several approaches to equilibrium headspace analysis. One of the newest static sampling approaches, solid phase microextraction (SPME), offers the greatest collection efficiency for the higher melting point compounds. Trace volatiles are collected by absorbing them in an appropriate solid phase that is supported on a 100-μm-diameter silica fiber. The SPME fiber is then injected into a gas chromatograph (GC), efficiently dispensing its contents at the GC column. Another technique, dynamic headspace analysis, is an off-the-shelf, automated technique that flushes a portion of the headspace volume via a heated capillary into the GC. These

instruments offer a more accessible approach to analyze less volatile compounds as their upper temperature range increases (e.g., 300°C).

In this application, we investigated both static and dynamic sampling approaches. With static collection, we were able to achieve a reproducibility of the fully saturated getter of 1.3%. A slightly lower reproducibility was achieved with the dynamic approach of 2.9%. This decreased precision is attributed to surface adsorption of the compound on the transfer line walls of the static headspace sampler.

New Analysis Approach

For analysis, we used gas chromatography/mass spectrometry (GC/MS) coupled to an infrared (IR) detector. This system provides the needed separation and structural data to distinguish the partially saturated isomers and deuterated isotopes amidst a complex matrix. Among the more interesting findings is an apparent hydrogen and deuterium exchange with the phenyl hydrogens when the getter reacts with an H_2/D_2 mixture. This exchange becomes apparent from the isotope distribution, which demonstrates a greater amount of deuteration than is stoichiometrically expected (i.e., 8/molecule). However, the average of the distribution yields the expected stoichiometic result. Our studies indicate that the hydrogen and deuterium exchange occurs only during the reduction step.

We initially intended to use the IR for the determination of hydrogen versus deuterium saturation; however, it became apparent that this information could be accurately deduced from the MS analysis. Fig. 1 shows several calibration curves obtained for the mole ratio of D_2/saturated DEB. The red curve is the theoretical calibration (assuming that the samples were accurately produced). We obtained good precision—however, we noticed that at increased levels of deuteration, the accuracy deviates from theoretical.

Because of its composite nature, the saturated DEB headspace concentration exhibits a trend similar to a Langmuir isotherm with increased percent saturation. In this case, a calibration curve or knowledge of the getter formulation would be needed for quantification of percent saturation. However, there appears to be a relationship between saturation and the relative amounts of partially saturated intermediates that would permit determining total percent saturation. From a limited set of standards, we were able to develop an empirical expression that describes this relationship. The advantage of this calibration approach is that it provides a more accurate percent saturation value that does not depend on the relative amount of unsaturated DEB, which is considerably less volatile that saturated DEB. For quantification, one would measure two isomers with similar vapor pressures. Fig. 2 shows a comparison of two calibration curves for a set of partially deuterated standards obtained by liquid extraction and dynamic headspace analysis.

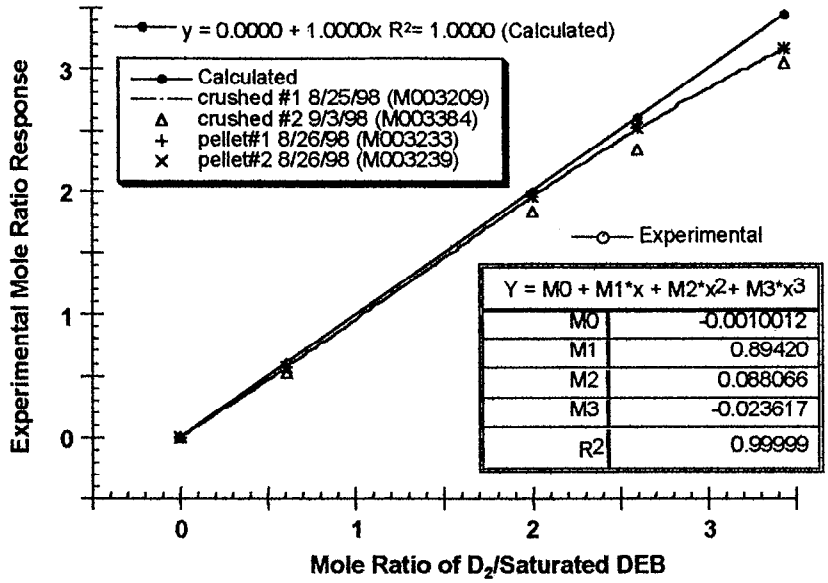


Figure 1. Headspace GC/MS analysis of saturated DEB with different H_2/D_2 mixtures. Calculated results assume accurate preparation of standards.

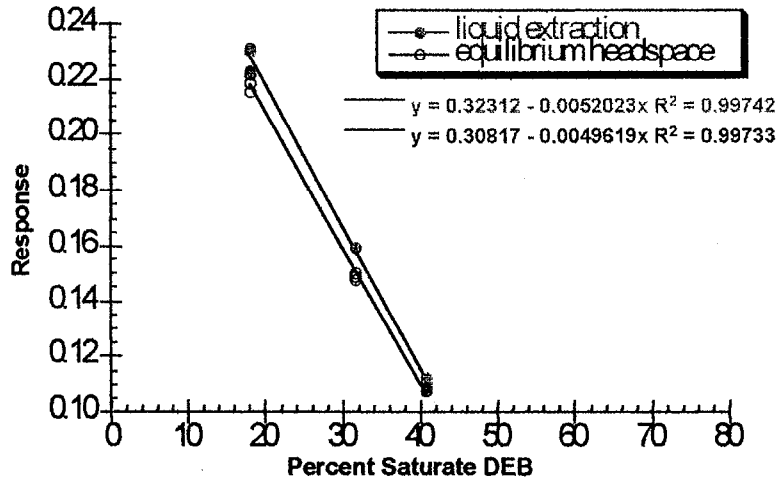


Figure 2. Comparison of similarity in response using liquid injection and equilibrium headspace sample introduction approaches. Response is proportional to the ratio of the fully saturated DEB to the 75% saturated cis isomer.

Conclusion

Solid phase microextraction and dynamic headspace sampling can provide high sampling precision of 1.3 and 2.9%, respectively for the saturated DEB getter. Using GC/MS analysis with headspace sampling, we can achieve high precision for both percent saturation and deuteration. Not only is this analysis approach accessible and cost effective, the sample is not consumed and can remain sealed in the headspace vial throughout the analysis.

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.